

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 17/00, 3/395, A61L 9/01		A1	(11) International Publication Number: WO 96/30491
			(43) International Publication Date: 3 October 1996 (03.10.96)
(21) International Application Number: PCT/GB96/00759		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 27 March 1996 (27.03.96)		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(30) Priority Data: 9506172.7 27 March 1995 (27.03.95) GB			
(71) Applicant (for all designated States except US): JEYES GROUP PLC [GB/GB]; Thetford Technical Centre, Brunel Way, Thetford, Norfolk IP24 1HF (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): NORMAN, Russell [GB/GB]; 9 Walsingham Mews, Rickingham, Diss, Norfolk IP22 1ET (GB). WILSON, Brian, Murie [GB/GB]; "Torridon", 52 Common Road, Bressingham, Diss, Norfolk IP22 2BB (GB). MARSHALL, John [GB/GB]; 27 Wentworth Green, Sunningdale, Norwich NR4 6AE (GB).			
(74) Agent: RUFFLES, Graham, Keith; Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB).			
(54) Title: HALOGEN-RELEASING COMPOSITION FOR LAVATORY CLEANSING			
(57) Abstract A solid lavatory cleansing composition comprises: (i) a halogen-release agent containing at least 30 mole % of active halogen; (ii) a substantially non-oxidizable, substantially anhydrous surfactant component; and (iii) a substantially non-oxidizable solubility retardant agent.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Larvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

HALOGEN-RELEASING COMPOSITION FOR LAVATORY CLEANSING

This invention is concerned with improvements in and relating to lavatory cleansing.

In particular, the present invention is concerned with solid lavatory cleansing compositions intended to be brought into contact with the flush water of a lavatory or urinal whereby a part of the composition is dissolved in the flush water to release active ingredients thereto for cleaning the lavatory or urinal. The compositions are immersed in the water cistern of a lavatory or urinal, either as free-standing blocks or may be placed or contained in a dispensing device, to be sited in a lavatory cistern. The invention is also concerned with lavatory cleansing compositions for intermittent contact with the flush water of a lavatory or urinal, e.g., a so-called "rim block" for placing in a container to be held under the rim of a lavatory, or else on top of a tank or cistern wash hand basin such as is common in Japan.

A desirable component of such blocks is a halogen release agent, that is a compound which on contact with water releases hypohalous acid and/or hypohalite ions to the water, since these are powerful sanitising and cleansing agents.

However, such compounds are highly reactive and hence may be difficult or even dangerous to incorporate in lavatory cleansing blocks. This is especially the case with the more highly reactive halogen release agents such as the halogenated hydantoins, halogenated glycolurils or trichloro-isocyanuric acid. These more highly active halogen-release components may be characterised by their halogen content, typically having an active halogen content of 30 mole%, or higher.

In particular, WO 94/18605 discloses a solid lavatory cleansing block comprising one or more anionic surfactants, a halogen release agent component and a solubility control agent. However, this does not teach how to form a stable block based on a halogen release component having an active halogen content of at least 30 mole%. Examples of blocks which contain such high halogen levels (i.e. DCDMH and

BCDMH) are described in EP-A-0 206 725. However, in practice it is not possible to achieve a sufficient degree of stability for commercial use with these particular formulations.

It has now been found, in accordance with the present invention, that halogen-release agents may readily be incorporated in certain lavatory cleansing compositions, as hereinafter defined.

According to the invention, therefore, there is provided a solid lavatory cleansing composition comprising:-

- (i) a halogen-release agent, containing at least 30 mole% active halogen;
- (ii) a substantially non-oxidizable, substantially anhydrous surfactant component; and
- (iii) a substantially non-oxidizable solubility retardant agent.

Thus, a particular non-limiting embodiment of the invention provides a solid lavatory cleansing block formed of a composition comprising (A) from 1 to 80%, preferably from 20 to 60%, by weight of the surface active component comprising one or more substantially anhydrous, substantially non-oxidizable anionic surface active agents; (B) from 1 to 90%, preferably from 1 to 50%, e.g. 1 to 30% by weight of halogen-release agent; and (C) from 1 to 50%, preferably from 1 to 30%, by weight of a substantially non-oxidizable solubility control agent (as hereinafter defined).

Examples of highly active halogen-release agents which may be employed alone or in combination in this system include:-

N,N'-dichloro-dimethyl-hydantoin (DCDMH-av. halogen 34 mole%), N-bromo-N'-chloro-dimethyl-hydantoin (BCDMH-av. halogen 48 mole%) and N,N'-dibromo-dimethyl-hydantoin (NBDMH-av. halogen 56 mole%), as well as other halogenated alkylated hydantoins, and trichloroisocyanuric acid (TCCA, av halogen 46 mole%), N,N,N,N-tetraglycoluril (av. halogen 50 mole%).

Suitable surface active agents for use in the composition of the invention are anionic surface active agents, especially alkali metal, typically sodium, alkyl sulphates (e.g. lauryl sulphate), primary and secondary alkane sulphonates or sarcosinates or mixtures thereof, provided that these are in substantially non-oxidizable and substantially anhydrous form. In this context, "substantially anhydrous" means that the

water content as expressed as the total of free and banded water in the surfactant is preferably less than 2% by weight of the surfactant sample, more preferably less than 1% by weight.

The solubility control agent should also be substantially non-oxidizable. It is selected from one or more such materials. Provided that this criterion is met, such agents may be virtually wholly insoluble in water or if, as discussed below a nonionic surface active agent, have a low HLB, e.g. 5 or less. Such agents being substantially non-oxidizable are substantially resistant to attack by the halogen release component, both in the composition and in aqueous solutions produced by dissolution of the composition in use. It is a matter of simple experiment to determine whether any candidate is so resistant. Generally, the solubility control agent should be a saturated organic material or a highly chlorinated organic material. Examples of solubility agents which may be employed include polyethylene waxes; saturated tertiary alcohols; paradichlorobenzene; and difficultly hydrolysable esters.

Provided that they meet the criterion of being substantially non-oxidizable, such solubility control agents may also be chosen from non-oxidizable organic liquids. A wide variety of these may be employed, such as mineral oils, liquid hydrocarbons (e.g. liquid alkanes), chlorinated hydrocarbons, silicone oils, liquid ketones (e.g. 2-decanone), liquid tertiary alcohols (e.g. 2-methyl-hexan-2-ol), and liquid esters e.g. simple esters such as methyl decanoate, and more complex esters such as glycerol, propylene glycol, triethylene glycol esters of C_8 - C_{10} fatty acids and/or succinic acid. Examples of such complex esters are those sold under the trade name Miglyol 812, Miglyol 829, Miglyol 840, Plasthall 4141, Crodamol GTCC, Crodamol PC and Radia 7108.

Particularly preferred examples of such solubility control agents include solid esters; waxes; saturated fatty acid esters; mineral oils; and polysiloxanes. It has been found that the use of a mixture of non-oxidizable solubility control agents may often prove useful. Thus a mixture of an essentially hydrocarbon material, such as paraffin wax and/or a mineral oil, with an ester of a fatty acid such as isononyl stearate or triethylene glycol caprate/caprylate, may be employed. Further, it is sometimes useful to employ, in admixture, a combination of both a solid and a liquid hydrocarbon

material. Other substantially non-oxidizable solubility control agents include glycolurils and inorganic compounds such as aluminium hydroxide.

As will be appreciated, any other ingredient present in the compositions of the invention (whether surfactant-containing or not) should be resistant to attack by the halogen release agent. Most perfumes which are commonly employed in lavatory cleansing blocks are also subject to attack by halogen-release agent although some odiferous materials may be adequately resistant (and additionally serve as solubility control agents). Adequately resistant examples of these include substituted quinolines, cedryl methyl ether and cineole. Many of these perfumes are suitable also to fulfil the role of the solubility control agent as well as to function as processing aids, e.g. in an extrusion process. Particular examples of perfumes include Citrus 4022 ex IFF, Pine 2363 ex IFF, Fantasy 2366 ex IFF, Artic Fresh 2662 ex IFF, and Oriental Fruits F540096 ex Quest.

Fillers, typically mineral fillers, may be present in the blocks and are suitably present in amounts of from 1 to 75% by weight, preferably 1 to 50% by weight, e.g. 1 to 30% by weight. The filler is often required to increase the density, life or integrity of the block and suitable examples are salts such as calcium sulphate and sodium sulphate, as well as clays such as laponite.

Lavatory cleansing blocks commonly contain a germicide or preservative but this is not generally necessary in the case of the blocks of the invention since they already contain a powerful germicide(s), namely the halogen-release agent.

Some insoluble pigments are resistant to halogen release agents and may be incorporated in the blocks of the invention to impart a coloration.

Suitable examples include inorganic pigments of mixed - phase types, consisting exclusively of metal oxides such as Co/Al oxide (blue) and Co/Ti/Ni/Zn oxides (Green). These can be conveniently incorporated in the blocks of the invention by dispersing in the powder mixture.

Solid blocks may suitably be formed by a compression process, especially an extrusion or tableting process. For extrusion, this comprises the steps of forming a mixture of the components of the composition, extruding this mixture into rod or bar form and then cutting the extruded rod or bar into appropriately sized pieces or blocks.

Alternatively, blocks may be prepared by a melting and casting process, e.g. one in which fusible components of the block are fuse melted, the non-fusible components adhere to the melt, and the resultant mixture cast into moulds.

When an extrusion process is employed the mixture to be extruded should contain up to 25% by weight, of a liquid component or a solid component which is liquefied under extrusion conditions to act as a processing aid. Suitable such liquids include hydrocarbons (e.g. liquid alkanes), polysiloxanes, chlorinated hydrocarbons, silicone oils, liquid ketones (e.g. 2-decanone), liquid tertiary alcohols (e.g. 2-methyl-hexan-2-ol), and liquid esters e.g. simple esters such as methyl decanoate, and more complex esters such as glycerol, propylene glycol, triethylene glycol esters of C₈-C₁₀ fatty acids and/or succinic acid. Examples of such complex esters are those sold under the trade names Miglyol 812, Miglyol 829, Miglyol 840, Plasthall 4141, Crodamol GTCC, Crodamol PC and Radia 7108. These liquid components can also serve as solubility control agents. Suitable liquefiable solid components include solid esters such as cetyl palmitate and these also can serve as solubility control agents

In order that the invention may be well understood the following examples are given by way of illustration only. All amounts are expressed as percentages by weight unless explicitly recited to the contrary. Typical block weights are from 25g to 150g e.g. from 30 to 120g.

Blocks having a weight of 50g were prepared by melting and casting the following composition:-

Constituents	Example 1
	% w/w
DBDMH	20
Sodium Lauryl Sulphate	25
Laponite	15
Paraffin Wax	10
Mineral Oil	15
Isononyl Stearate	15

Where:-

DBDMH is dibromodimethylhydantoin in powder form ex Peboc.

Laponite is a smectite type clay.

The following were prepared by an extrusion process:-

Constituent	Example						
	2	3	4	5	6	7	8
			% w/w				
Hostapur SAS93 (2.0% w/w MgO)	58.80	-	n/a	-	-	-	-
Hostapur SAS93 (0.5% w/w MgO)	-	50.0	-	-	-	-	-
Hostapur SAS93 (1.0% w/w CaSO ₄)	-	-	-	-	-	50.0	-
Hostapur SAS93 (5.0% w/w MgO)	-	-	41.0	40.9	40.9	-	54.0
Calcium Sulphate	13.7	21.0	18.0	18	18	23.0	25.0
Plasthall 4141	4.90	3.0	7.0	7.0	7.0	-	-
Crodamol MM	5.90	9.0	-	-	-	7.0	-
Halogen G	16.70	17.0	17.0	-	-	15.0	15.0
Citrus 4022	-	-	-	-	-	5.0	6.0
Cetyl Palmitate	-	-	17.0	17.0	17.0	-	-
Sicopal Blue K6310	-	-	-	0.1	-	-	-
Sicopal Green K9710	-	-	-	-	0.1	-	-
Dantobrom RW	-	-	-	17.0	-	-	-
Biolab Bromicide	-	-	-	-	17.0	-	-
Rimstick/Ontank Block (50g)	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Intank block (60g)	No	No	Yes	Yes	Yes	Yes	Yes

Where:-

- Hostapur SAS 93 is a 93% active secondary alkane sulphonate in powder form, incorporating inorganic salts as declared (balance is sodium sulphate) ex Hoechst.
- Halogen G is a 92% active BCDMH in granular form, incorporating boric acid and sodium chloride as declared ex Rohm & Haas.
- Dantobrom RW is a combination of BCDMH, DCDMH and DCEMH in powder form ex Lonza Inc.
- Plasthall 4141 is triethylene glycol caprate caprylate in liquid form ex CP Hall.
- Biolab Bromicide is a 100% active BCDMH in powder form ex Great Lakes Chemical (Europe) Ltd.
- Crodamol MM is myristyl myristate in solid form ex Croda Chemicals.
- Citrus 4022 is a suitable fragrance ex IFF.
- Sicopal Blue K6310 is a Co/Al oxide pigment in powder form ex BASF.
- Sicopal Green K9710 is a Co/Ti/Ni/Zn oxide pigment in powder form ex BASF.

Constituents	9	10
	% w/w	
Hostapur SAS93 (5% w/w MgO)	39	-
Cetyl Palmitate	17.0	-
Calcium Sulphate	18.0	18.0
TCCA	17.0	-
Plasthall 4141	9.0	5.0
Crodamol SS	-	20.0
Hamposyl L95	-	35.0
Halogen G	-	17.0
Citrus 4022	-	5.0
Rimstick/Ontank block (50g)	Yes	Yes
Intank	Yes	Yes

Where:-

TCCA is 100% active trichloroisocanuric acid in powder form ex Chlorchem.

Crodamol SS is a blend of synthetic fatty acid esters in powder form ex Croda Chemicals.

Hamposyl L95 is 95% active sodium lauryl sarcosinate in powder form ex Hampshire Chemicals.

CLAIMS:

1. A solid lavatory cleansing composition comprising:
 - (i) a halogen-release agent containing at least 30 mole% of active halogen;
 - (ii) a substantially non-oxidizable, substantially anhydrous surfactant component; and
 - (iii) a substantially non-oxidizable solubility retardant agent.
2. A composition according to claim 1, comprising (A) from 1 to 80% by weight of the surface active component, (B) from 1 to 90% by weight of halogen-release agent; and (C) from 1 to 50% by weight of the substantially non-oxidizable solubility control agent.
3. A composition according to either preceding claim, wherein the halogen release agent comprises an halogenated alkylated hydantoin.
4. A composition according to claim 3, wherein the halogenated alkylated hydantoin comprises one or more agents selected from N,N'-dichloro-dimethyl-hydantoin, N-bromo-N'-chloro-dimethyl-hydantoin, and N,N'-dibromo-dimethyl-hydantoin.
5. A composition according to any preceding claim, wherein the halogen release agent comprises trichloroisocyanuric acid.
6. A composition according to any preceding claim, wherein the halogen release agent comprises N,N,N,N-tetraglycoluril.
7. A composition according to any preceding claim, wherein the substantially non-oxidizable, substantially anhydrous surfactant component comprises an anionic surfactant.

8. A composition according to any preceding claim, wherein the anionic surfactant is selected from one or more alkyl sulphates, primary and secondary alkane sulphonates and sarcosinates, and salts thereof.
9. A composition according to any preceding claims, further comprising from 1 to 75% by weight of a mineral filler.

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/GB 96/00759

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D3/395 A61L9/01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 206 725 (JEYES GROUP) 30 December 1986 cited in the application see page 6, paragraph 2-3; claims 1-7; table 1	1-5,7-9
X	--- WO,A,92 18605 (JEYES) 29 October 1992 cited in the application see page 3, paragraph 2 - page 5, paragraph 2	1,2,5,7, 8
X	--- GB,A,2 273 106 (JEYES GROUP PLC) 8 June 1994 see page 4, paragraph 2 - page 5, paragraph 1; claims 1-4 -----	1,2,5,7, 8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the international search

11 July 1996

Date of mailing of the international search report

19-07-96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patendaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Van Bellingen, I

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No
PCT/GB 96/00759

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP-A-206725	30-12-86	AU-B-	585356	15-06-89
		AU-B-	5887486	18-12-86
		CA-A-	1300464	12-05-92
		DE-D-	3689368	20-01-94
		DE-T-	3689368	23-06-94
		GB-A,B	2178442	11-02-87

WO-A-9218605	29-10-92	AT-T-	128181	15-10-95
		AU-B-	667039	07-03-96
		AU-B-	1982192	17-11-92
		BR-A-	9205926	05-07-94
		CA-A-	2108975	23-10-92
		DE-D-	69204997	26-10-95
		DE-T-	69204997	11-04-96
		EP-A-	0581826	09-02-94
		ES-T-	2080497	01-02-96
		GB-A,B	2270084	02-03-94
		HK-A-	177395	01-12-95
		JP-T-	6506711	28-07-94
		NZ-A-	242448	27-04-94

GB-A-2273106	08-06-94	AU-B-	5431594	22-06-94
		CA-A-	2150458	09-06-94
		EP-A-	0672103	20-09-95
		WO-A-	9412612	09-06-94
		GB-A-	2288814	01-11-95
		ZA-A-	9308634	01-08-94
